Normal vibration of polybenzamide

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A normal vibrational spectroscopic analysis has been carried out for polybenzamide for both *cis–trans* and all-*trans* structures. The valence force field suitable for non-redundant coordinates was taken from several earlier studies. The calculated values coincide well with the experimental data including the polarization observations. Several vibrations above $1000\,cm^{-1}$ were found to be sensitive to changes in intermolecular interactions. The changes in these specific vibrations have been interpreted as originating from the electronic redistribution of the cross-conjugated backbone, directly related to changes in the hydrogen bond interactions. The potential energy terms associated with the backbone stretching vibrations are found to be perturbed significantly. The theoretical moduli of two molecular crystals involving both the *cis–trans* and the all-*trans* conformations have been calculated.

(Keywords: polybenzamide; normal coordinate analysis; i.r. spectra)

INTRODUCTION

Fibres of polybenzamide (PBA) can be spun from the liquid crystalline state to possess exceedingly high modulus and strength, comparable to fibres of poly(*p*-phenylene terephthalamide) (PPTA) or Kevlar$^{TM\,1-5}$. The crystal structure, macroscopic mechanical properties, molecular weight, viscosity and phase transition of PBA have been studied extensively[1–5]. Although vibrational spectroscopy has often been used to characterize polymer structures, to our knowledge, only a few vibrational spectroscopic analyses have been carried out on PBA[5]. This is apparently due to the lack of definitive structural analyses and reliable force constants. In most cases, especially when cyclic redundancy is present, high correlation between the force constants exists making refinement of force field difficult if not impossible to carry out. In order to overcome these difficulties, we have established a particular set of non-redundant coordinates for the polymer based on various small model molecules. We have also taken a set of force constants based on these non-redundant coordinates, used previously to analyse PPTA[6], to calculate the i.r. bands observed for PBA. We found that many vibrations are extremely sensitive to changes in temperature. It is difficult to explain these changes, as they are usually considered to be localized backbone vibrations. However the frequency shifts could be correlated with the electronic redistribution on the whole molecular backbone. The crystallite moduli of PBA for both the *cis–trans* and the all-*trans* conformations have been calculated from the force field.

EXPERIMENTAL

The oriented film was prepared by shearing the PBA solution between two glass slides. PBA powder was dissolved in 98% H_2SO_4 to form a concentrated solution (9% wt/wt) which was in the anisotropic mesophase region. The solution was then sheared by two glass slides to form an oriented film and the sandwich-like assembly was put into water which was used as coagulant for PBA. The film was then washed with distilled water and dried in a vacuum oven at room temperature.

The non-oriented film prepared as described above without being sheared was heated to 404°C and cooled to -150°C in a specially constructed heating cell.

The i.r. spectra of the films were recorded with an IBM IR/32 spectrometer (*FT*i.r.) using a resolution of $2\,cm^{-1}$ and 256 scans.

RESULTS AND DISCUSSION

Normal coordinate analysis

The i.r. spectra of PBA are shown in *Figure 1*, together with the polarized spectra, parallel and perpendicular to the chain axis of the molecules. The molecular structure of PBA in the crystalline state, shown schematically in *Figure 2a*, was determined by X-ray diffraction[1]. *Figure 2* shows the *cis–trans* conformation defining the relative orientation of the phenylene rings and amide groups, together with the all-*trans* conformation suggested earlier by Hasegawa *et al.*[1]. For the *cis–trans* structure, the only symmetry element is a two-fold screw axis. Its point group is isomorphic to C_2 with 80 vibration modes divided into 40a and 40b units. The two species should be correlated to the observation of the polarized optical properties of the i.r. bands of PBA. When the vibration mode belongs to species a, the transition moment vector of the mode is along the polymer chain axis. For the other species, the transition moment vector is normal to the chain. Therefore, most of the observed spectral bands can be well assigned to these symmetry species, as shown in *Table 1*.

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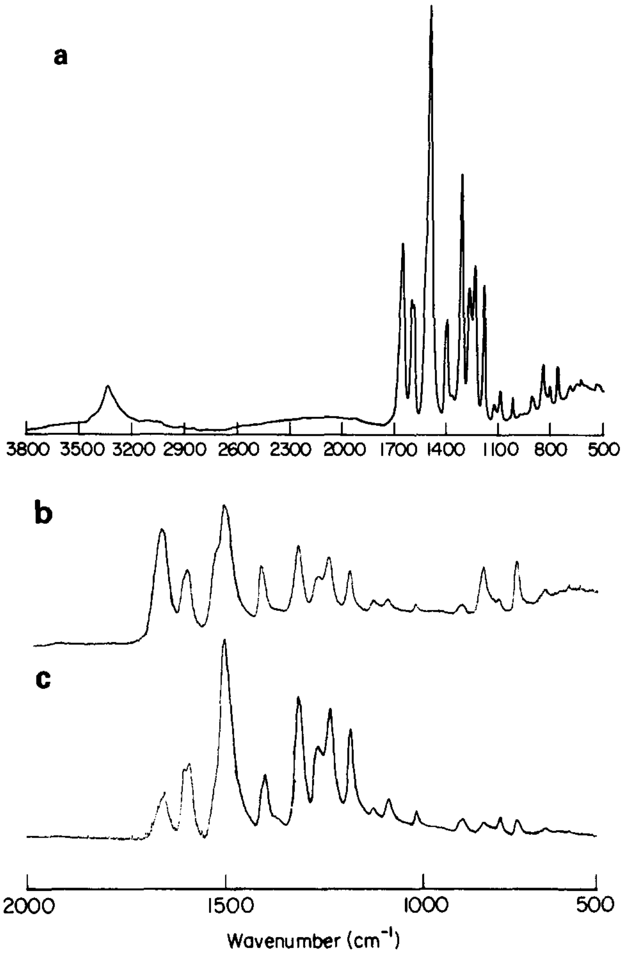

Figure 1 I.r. spectra of PBA: (a) non-oriented film; oriented film recorded with the polarizer (b) perpendicular and (c) parallel to the orientation

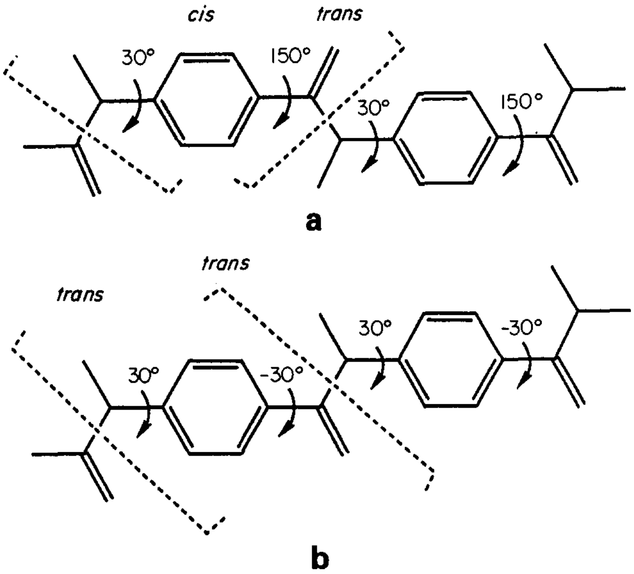

Figure 2 Conformations along the polymer chain of PBA: (a) *cis–trans*; (b) all-*trans*

Table 1 Observed and calculated band frequencies of PBA for the *cis–trans* conformation

Obs.		Dichroism	Calc.		
I.r. intensity			a	b	PED
3346	s	σ	3345	3345	t(99)
3062	w		3062	3062	r(99)
			3059	3059	r(99)
3036	w		3040	3040	r(100)
			3039	3039	r(100)
1662	s	σ		1653	S(57), R(19), R′(15), δ′(13)
			1649		S(64), δ′(15), R′(15), R(12)
				1613	R(58), r″(11), β(10), θ(10)
1605	s	π	1612		R(65), β(15), RAD1(12)
				1591	R(55), β(14), θ(13)
1593	s	π	1590		R(68), β(10), S(10)
1527	s	σ		1548	θ(37), R′(20), R(20)
			1543		R(36), β(21), r′(11)
1507	vs	π	1511		β(50), R(34), r′(11)
				1486	β(41), R(24), θ(23), R′(10)
1410	s	σ		1407	R(44), β(34)
1402	s	π	1384		β(42), R(41)
1319	vs	π	1335		β(54), θ(16), R(14)
				1321	β(47), R(35), θ(13)
				1314	β(52), R(50)
1272	s	π	1299		R(77), β(35)
				1263	R(83), θ(20), β(11), r″(10)
1238	vs	π	1262		R(39), θ(20), β(18), r″(17)
				1233	r′(39), R(29), β(15)
1186	s	π	1188		β(80)
				1187	β(77)
				1106	R(20), RTD(19), R′(19)
1127	m	π	1102		β(44), R(35)
				1101	β(52), R(37)
1091	ms	π	1084		R(42), R′(16)
1019	m	π	1014		RTD(41), R(35), β(14)
				1013	RTD(45), R(33), β(12)
972	vw		963	963	γ(125), RAT2(12)
			960		γ(130), RP(58)
950	vw	σ		953	γ(134), RP(46)
				887	γ(48), RAT1(18), γ′(15), γ″(12)
909		π	877		R(21), δ(14), γ(15), δ′(10)
				859	γ(18), δ′(17), δ(11), γ″(10)
			847		RP(39), γ′(27), γ(17), τ2(13), μ′(12)
847	s	σ	838	838	γ(113)
				831	R(50), RAD1(15), r′(11)
			822		γ(71), γ′(18), RP(13), RAT1(12)
807	m	π	774		r′(17), θ′(16), RTD(15)
764	m	σ		769	RP(89), γ′(22), γ″(19), μ(17)
701	w				
691	w	σ		698	γ(56), τ2(15), μ′(12), RP(12), γ′(10)
			684		μ′(27), RAD1(13)
			675		μ′(25), RAD1(21)
				666	RP(47), μ′(30), μ(16)
631	w		644		RAD2(77)
				643	RAD2(73)
601	vw		616		RP(71), μ(12)
				585	θ′(20), RAD1(19), RP(14)
539	w		534		RP(24), RAT1(19), δ′(16)
486	w		466		RAT1(66), γ′(34), γ″(21)
				446	RAT1(46), γ″(17), γ′(16), RAD1(16)
383			401	401	RAT2(160)
				373	β″(12), r′(11)
				364	RAD1(27), r″(23), RAT1(21)
336			336		θ′(38), β′(18), δ(14)
305				311	β′(36), μ(17), δ′(12), θ′(10)
				265	γ″(26), γ′(17), β″(11)
240			262		μ(67), τ2(25), γ′(14), γ″(14), μ′(10)
				195	β″(28), μ(24), τ2(21)
				174	τ2(41), μ(36), RAT1(19), δ(16)
			157		β″(39), β′(20)
			94		RAT1(29), γ″(22), τ2(20), μ(11)
			76		δ(38), δ′(23), β″(11)
			66		τ2(68), μ(26), γ′(24), RAT1(11)
			28		τ3(49), τ1(48)
				25	τ3(49), τ1(48)
				19	τ1(50), τ3(49)

Due to the lack of fundamental studies on the molecular force field of complicated aromatic compounds, no well defined force constants suitable for the aromatic polyamides are available. An effort has recently been made, in which three kinds of vibrational force

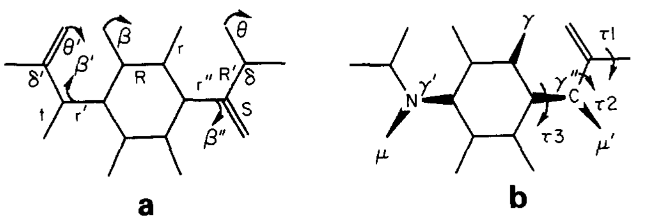

Figure 3 Internal coordinates for PBA: (a) stretchings and in-plane bendings; (b) out-of-plane bendings and torsions

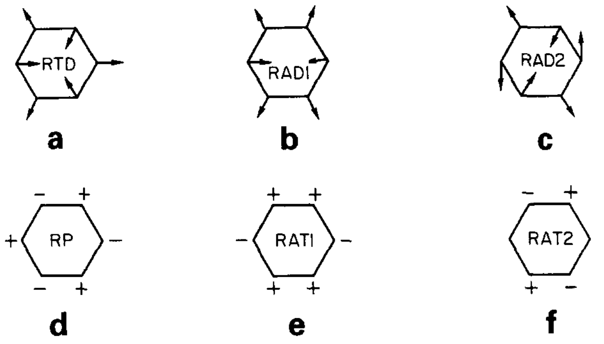

Figure 4 Non-redundant internal coordinates for the phenylene of PBA: (a) ring trigonal deformation; (b) ring asymmetric deformation type 1; (c) ring asymmetric deformation type 2; (d) ring puckering; (e) ring asymmetric torsion type 1; (f) ring asymmetric torsion type 2

constants, that is, for the amide group in polypeptides (force field I)[7], for the benzene ring (force field II)[8] and for the connecting bonds to the ring in monosubstituted benzene rings (force field III)[9], were combined to analyse the normal coordinate vibrations of PPTA[6]. Quite good agreement was found between the calculated frequencies and the observed spectral bands; this led us to apply such force field treatment to PBA. The values for bond lengths and angles, the internal coordinates used in this analysis, and the force constants have been taken from a study of Kevlar[6]. For clarity, the internal coordinates are depicted in *Figures 3* and *4*. The calculated vibrations and the potential energy distributions (PED) are listed in *Table 1*.

The agreement between the calculated and observed frequencies was not perfect but acceptable. Most of the deviations for these vibration modes are less than a few wavenumbers (see *Table 1*). The maximum deviation, 807 cm^{-1} (obs.) *versus* 774 cm^{-1} (calc.), amounts to 33 cm^{-1}, which reflects some weaknesses of the combined force field. The i.r. spectral bands of amide I and amide II are generally around 1640 and 1550 cm^{-1} for nylons[10], and 1650 and 1550 cm^{-1} for polypeptides[7]. In the case of PBA, the two characteristic bands appear at 1662 and 1527 cm^{-1}, as the substitution of the benzene ring to the amide group[11]. Obviously, the calculated frequencies, 1653 and 1548 cm^{-1}, are still around the original vibration energies copied from force field I for polypeptides, as mentioned above. Another deviation of the 1127 cm^{-1} (obs.) *versus* 1102 cm^{-1} (calc.) assigned as the C–H in-plane bending of the ring (β) coupled with the C=C stretching of the ring (R), implies that force field II is not good enough for PBA. This quite possibly results from the different substituents on both sides of the ring in the PBA chain. Their different capacities to conjugate with the π system of the ring, cause an asymmetrical charge distribution in the skeletal ring. Thus, the force field of the moiety of the ring in the PBA chains loses its symmetrical centre, which remains in the PPTA ring. Therefore, force field II featuring a symmetrical centre, is unlikely to describe the vibration modes for PBA as good as for PPTA. Other weaknesses can also be found in a few of the other larger deviations. Consequently, an understanding of the combined force field in the PBA system or for aromatic polyamides has primarily been obtained. Under this situation, there does not seem to be enough experimental data to make a new set of force constants for aromatic polyamides. As shown in *Table 1*, the experimental data of PBA can be assigned quite well to the normal vibrations under the combined force field to a good approximation.

Crystallite modulus

Using reliable force constants, the crystallite modulus of a polymer can be calculated by several methods[12–14]. One of the easiest and most straightforward methods is to calculate the dispersion curve for the acoustic vibration. If the frequency, $\tilde{\nu}$, is proportional to the wavevector or to the phase difference, θ, between adjacent translational repeats, an approximation usually appropriate for long chains, the square root of the modulus can then be considered as being proportional to the slope of the $\tilde{\nu}(\theta)$ plot. We calculated the frequencies in the first Brillouin zone with phase differences of 2.5°, 3°, 4°, 5°, 6° and 10° for the *cis–trans* conformation, and 2°, 3°, 4° and 10° for the all-*trans* conformation. The crystallite moduli for the *cis–trans* and the all-*trans* chains obtained were 143 and 216 GPa, respectively.

The much lower modulus for the *cis–trans* conformation could be understood from a comparison of the potential energy distribution in force constants (PEF) between the two conformers of an acoustic vibration mode, say for a small phase difference of 3°, as shown in *Table 2*. This vibration describes a molecular deformation during the transition between vibrational states, that is the same as a deformation of PBA chains under an external stress along the chain axis. PEF depicts a feature of the deformation, distributed into different chemical structure units, as defined by internal coordinates. In *Table 2*, relatively smaller values are found for the *cis–trans* conformer for the first five internal coordinates, and relatively larger values for the other coordinates. It is to be noted that all of the first five internal coordinates

Table 2 Comparison of the potential energy distribution in force constants (PEF) between the *cis–trans* and the all-*trans* conformational sequence of the acoustic mode (phase difference = 3°)

Internal coordinate	Force constant	PEF	
		cis–trans	all-*trans*
r'	5.043	6.5	10.4
r''	4.409	8.4	12.2
R'	6.415	0.3	2.1
R	6.500	3.6	5.0
RAD1	1.236	17.1	26.0
δ	0.6205	14.7	11.6
δ'	1.3478	7.4	11.8
β'	0.8375	7.6	1.1
β''	0.8375	7.3	4.8
RAT1	0.3863	4.7	0.0
γ	0.5852	3.6	0.1
γ'	0.6581	6.3	2.0
γ''	0.6581	6.1	3.4

Table 3 Band shifts and force constant changes during cooling from 404 to 13°C

Band (cm^{-1})	Δf (cm^{-1})	Jacobian elements for the internal coordinates					Calc. Δf (cm^{-1})
		R	r′	r″	R′	S	
1238	5.1	39.673	9.505	23.907	2.830	1.014	6.53
1593	5.1	83.411	1.846	0.077	7.070	8.655	5.36
1319	5.6	19.389	0.938	9.952	1.897	1.018	2.84
1605	6.5	81.597	11.267	17.613	3.941	1.282	6.13
1507	7.5	40.453	16.055	2.917	1.515	0.791	6.93
1272	8.9	77.918	5.111	4.071	4.582	0.016	9.26
K_j		−0.14	0.50	−0.10	3.99	−1.37	

Table 4 Band shifts and force constant changes during cooling from room temperature to −150°C

Band (cm^{-1})	Δf (cm^{-1})	Jacobian elements for the internal coordinates					Calc. Δf (cm^{-1})
		R	r′	r″	R′	S	
1238	2.9	39.673	9.505	23.907	2.830	1.014	3.87
1593	3.7	83.411	1.846	0.077	7.070	8.655	3.88
1319	4.1	19.389	0.938	9.952	1.897	1.018	2.23
1605	1.7	81.597	11.267	17.613	3.941	1.282	1.45
1507	3.6	40.453	16.055	2.917	1.515	0.791	3.21
1272	5.3	77.918	5.111	4.071	4.582	0.016	5.54
K_j		−0.19	0.37	−0.11	4.18	−1.18	

belong to the bond stretching force constants, which are more than one order of magnitude larger than the other force constants. Evidently, the more energy dissipated in bond stretching, the stronger the external force which can be borne. For the all-*trans* conformer, having larger PEF for the bond stretching force constants, it is reasonable to possess a larger modulus. In contrast, the *cis–trans* conformer (with smaller PEF) is only able to withstand a smaller stress along the chain during deformation of the molecular frame. It is also quite interesting to note that for the five coordinates the PEF ratios of the *cis–trans* to the all–*trans* are in the range 0.6–0.7, which roughly equals the modulus ratio 143/216 = 0.665. The other significant point found in the comparison is that different images of the deformations between the conformers can be described. In the third group of the data in *Table 2*, the corresponding internal coordinates belong to out-of-plane bendings. In particular, RAT1 is an out-of-plane bending of the phenylene ring, which shows a perpendicular displacement of the ring skeleton to the chain axis. As a result of this comparison, larger PEF values are found for the *cis–trans* conformer, describing a lateral displacement of the ring skeleton which occurs during the deformation of the *cis–trans* conformer during vibration or under applied external stress. In the case of the all-*trans* conformer, the PEF value for RAT1 is zero, thus indicating that no significant lateral motion of the rings would occur during deformation of the conformer.

Band shift and intermolecular interaction

When samples were cooled from 404°C to room temperature, the amide I band at $\sim 1662\,cm^{-1}$ shifted downwards by $2\,cm^{-1}$ and the bands of 1238, 1272, 1319, 1507, 1593 and $1605\,cm^{-1}$ shifted upwards by $>5\,cm^{-1}$. The largest shift was $\sim 9\,cm^{-1}$. These observations are shown in *Table 3*. Quite similar frequency shifts were observed when samples were cooled from room temperature to −150°C (*Table 4*). Since the rigid molecular chains have relatively little mobility, their conformations are not expected to change with temperature. An increase of intermolecular interaction, especially between the hydrogen bonds, is the probable cause for the observed frequency shifts.

Somewhat surprising is the fact that all the bands with significant temperature dependence mainly involve backbone stretching vibrations (C=C, C–C′, C′–N, N–C). We assume that the frequency shifts arise from changes in the potential energy terms, i.e. force constants, and not from changes in the kinetic energy term. Since cross-conjugation is the main mechanism stabilizing the chain backbone, the electronic redistribution of the backbone may be characterized by the weakening or strengthening of the stretching force constants. From our observation, the stretching force constants are the ones most perturbed by changes in intermolecular interactions.

As a first-order approximation, we consider only the changes in the stretching force constants for the frequency changes of normal vibrations. In theoretical normal vibrational analysis, if this approximation is made, the relationship between the shifted frequency and the increment of the stretching force constants is given by:

$$\nu_i = \nu_i^0 + \sum_j \frac{\partial \nu_i}{\partial K_j} \Delta K_j$$

where the partial derivatives are the Jacobian elements which can be obtained as part of the normal coordinate analysis. From this equation, the calculated increments and the related Jacobian matrix elements for the vibrations of interest are listed in *Table 3*. The change in the force constants is no more than 2–3% of the original values for $K_{C=C}$, $K_{C-C'}$ and K_{N-C}. Much larger changes occur for the other two force constants ($K_{C=O}$

and $K_{C'-N}$). The negative increment for $K_{C=O}$ accurately predicts the increase in the hydrogen bonding interaction as observed for the amide I band. The positive increment for $K_{C'-N}$ indicates that the C′–N bond tends to have more double bond character when the hydrogen bond is stronger.

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